

Adsorption of polydisperse polymer chains

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Abstract

The adsorption of polydisperse ideal polymer chains is shown to be sensitive to the large N tail of the distribution of chains. If and only if the number of chains decays more slowly than exponentially then there is an adsorption transition like that of monodisperse infinite chains. If the number decays exponentially the adsorption density diverges continuously at a temperature which is a function of the mean chain length. At low coverages, chains with repulsive monomer–monomer interactions show the same qualitative behaviour.

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Synthetic polymers are almost inevitably polydisperse. The polymer chains are not all of the same length, and so a polymer is not a single component but a mixture of chains of different lengths. However, almost all of the large number of theoretical studies of polymer adsorption have considered monodisperse polymer chains, where the chains are all of the same length. This is done to simplify matters and is a reasonable approximation when, as is often the case, the width of the distribution of lengths of polymer chain is small. Here we study polymers in which there are polymer chains with a very wide range of lengths, paying particular attention to the longest polymers in the distribution. Our motivation is not just the experimental fact that synthetic polymers are polydisperse yet are almost invariably treated within theory as being monodisperse. Polydisperse polymers may, and we show that they do, exhibit behaviour which is qualitatively different from that of monodisperse polymers. We study a very highly idealised model of polymer adsorption: ideal chains adsorbing onto a wall due to a short-ranged attraction between the wall and the monomers. This problem has been extensively studied for monodisperse chains [2–6], but not as far as the author is aware for polydisperse chains.

The adsorption of an ideal chain is a textbook problem. It is highly idealised: almost invariably the density of polymer adsorbed onto a surface is too high for interactions between the polymer segments to be neglected. However, it has served well as a simple first model of adsorption of monodisperse polymer chains [2] and we shall use it as such for polydisperse chains. There has been previous work within the Scheutjens–Fleer theory [7], on the adsorption of polydisperse polymer chains but not, as far as the author

is aware, on ideal chains. Roefs *et al.* [7] did not consider the large N tail of the distribution and so did not find the behaviour we will describe below. Note that in ref. [7] the ratio between the volume of the solution and the surface area of the wall was only of the order of the radius of gyration of the polymers. By contrast here we study a wall in contact with a bulk polymer solution so the ratio between the volume and surface area is infinity.

We start by briefly reviewing the behaviour of monodisperse chains, with particular emphasis on the dependence of the adsorption on the length of the chain. The chains are ideal and each consists of a linear chain of N monomers of length a . The chains are at a non-zero number density ρ in the bulk. The bulk polymer solution is in contact with a wall. This wall attracts monomers via a short-ranged attraction; the range is taken to be a for simplicity. The strength of attraction is ϵ . Having discussed monodisperse chains we then generalise the theory to describe an arbitrary polydisperse mixture of chains of differing lengths. We show that not all polydisperse mixtures behave in the same way: there are three qualitatively different behaviours possible. Which behaviour a mixture exhibits depends on the large N tail of the distribution. This is also true of the cloud-point curve of polydisperse polymers, as was shown by Šolc [8]. Recent work by the author on the bulk phase behaviour of polydisperse hard spheres [9] has found a similar sensitivity to the tail of the distribution.

Ideal chains do not interact with each other and so finite ideal chains are independent systems with a finite number of degrees of freedom. They therefore cannot exhibit a phase transition. For ideal chains there is only an adsorption transition in the limit that the number of monomers N

tends to infinity. We denote the transition temperature of infinite chains by T_a . For finite chains there is only a steep increase in the adsorbed density near T_a . Most distribution functions for polydisperse mixtures tend to zero only at infinity (e.g., the Schulz and distribution [1, 10]), which is to say that they contain an infinitesimal density of infinitely large chains. The question then arises: as there are infinitely long chains present is there a phase transition?

Below the adsorption temperature T_a large chains, $N \rightarrow \infty$ are adsorbed onto the wall. The chains form a layer of height D which can be easily estimated using a scaling argument due to de Gennes [2]. We restrict ourself to the weak-adsorption regime [2] where $D \gg a$. The free energy of adsorption of a single ideal chain has two competing parts. The first is the entropy change when a polymer chain is confined to a layer of height D , this scales as $-Na^2/D^2$. We take Boltzmann's constant to be equal to unity. The second is the energy change due to adsorption, this is $-N\epsilon$ times the fraction of monomers within the range of wall's attraction a/D . So, the free energy of adsorption ΔF is given by

$$\Delta F \sim T \frac{Na^2}{D^2} - N\epsilon \frac{a}{D}. \quad (1)$$

The width D of the layer at equilibrium is found by minimising ΔF

$$D \sim a(T/\epsilon), \quad (2)$$

which gives an adsorption free energy of

$$\Delta F \sim -N\epsilon^2/T. \quad (3)$$

An exact treatment of adsorbed ideal chains yields [3–6]

$$\frac{\Delta F(N)}{T} \sim -N(\epsilon/T - \epsilon/T_a)^2 \quad T < T_a, \quad (4)$$

which is the dominant part of the free energy difference between a chain in the bulk and a chain with one end near the wall, when both N and $|\Delta F|$ itself are much larger than unity but we are still in the weak-adsorption regime so $\epsilon/T - \epsilon/T_a$ is small. For large chains, the free energy difference ΔF between a chain adsorbed onto the wall and one in the bulk increases linearly with N .

Given ΔF we can follow the adsorption by the number density of chains adsorbed at the wall. Because the chains are ideal their density in the presence of an external field is just the bulk density times a Boltzmann weight $\exp(-\Delta F/T)$. The free energy ΔF given by eq. (4) is the exact form for a polymer chain which has one end at the wall. Thus the density of polymer chains with at least one end near the wall is

$$\rho_a \sim \rho \exp(-\Delta F/T) \quad (5)$$

$$\sim \rho \exp[N(\epsilon/T - \epsilon/T_a)^2] \quad T < T_a. \quad (6)$$

We can think of other densities such as the number density of monomers within a of the wall or the number density within the whole adsorbed layer, but both these densities behave in qualitatively the same way (as a function of temperature) as ρ_a . Above the adsorption transition, $T > T_a$,

the density near the wall is less than in the bulk, and tends to zero close to the wall for infinitely long chains. In the $N \rightarrow \infty$ limit then, there is an, infinite, jump in ρ_a at T_a : there is a thermodynamic transition at $T = T_a$. For finite N there is a sharp increase in ρ_a near $T = T_a$ but no transition.

The generalisation to polydisperse ideal chains is easy. In the bulk the density of polydisperse chains of different lengths N is determined by a distribution function $x(N)$. The number density of chains of length N is $\rho x(N)dN$ [10], where x is normalised

$$\int_0^\infty x(N)dN = 1 \quad (7)$$

so that the total number density of chains is ρ as before. Thus the density of monomers of chains of length N near the wall is $\rho x(N) \exp[-\Delta F(N)/T]dN$ and so the adsorbed density ρ_a when the polymer chains are polydisperse is given by the obvious generalisation of eq. (6),

$$\rho_a \sim \rho \int_0^\infty x(N) \exp[-\Delta F(N)/T]dN \quad T < T_a. \quad (8)$$

This is a definition, to obtain the behaviour we insert the free energy expression eq. (4) which is asymptotically exact in the $N \rightarrow \infty$ limit, in the weak adsorption regime. This is sufficient as it is the behaviour in this limit that determines whether or not there is an thermodynamic transition — finite chains cannot contribute to a discontinuity in ρ_a or its derivatives. So, using eq. (4) in eq. (8)

$$\rho_a \sim \rho \int_0^\infty x(N) \exp[N(\epsilon/T - \epsilon/T_a)^2] dN \quad T < T_a. \quad (9)$$

For monodisperse infinitely long chains then the adsorbed density is infinite below T_a . We see that for polydisperse chains this is also true if the integral of eq. (9) does not converge, which it does not whenever $x(N)$ decays more slowly than exponentially with N or it does decay exponentially like $\exp(-bN)$ (b positive) but $b < (\epsilon/T - \epsilon/T_a)^2$. So, if the decay of $x(N)$ is slower than exponential, e.g., log-normal or power law, then polydisperse chains behave as infinitely long chains below T_a . There is therefore an adsorption transition at T_a . If the decay of $x(N)$ is faster than exponential then there are not enough of the infinitely long chains to cause a transition and ρ_a increases sharply but does not diverge. An analogous dependence on $x(N)$ is found in the cloud-point curve of a polymer solution [8]. There if the decay is slower than exponential, the cloud-point curve occurs at the same effective temperature as that for infinite polymers. As here a slower than exponential decay means that the density of infinitely long polymers is high enough to cause the polydisperse solution to behave as a solution of infinite monodisperse polymer. The similarity in behaviour between the cloud-point curve and the results presented here is due to the fact that the free energy which determines the partitioning of the polymer at the cloud-point curve is also linear in N .

But the most interesting case is that of an exponential decay. There the behaviour is not like that of any monodisperse polymer. Consider a simple exponentially decreasing distribution function

$$x(N) = \bar{N}^{-1} \exp(-N/\bar{N}) \quad (10)$$

where \bar{N} is the average length of the polydisperse chains. The exponential distribution is a special case of the widely used Schulz distribution [1]. Inserting the distribution function eq. (10) into eq. (9) for the adsorption we obtain

$$\rho_a \sim \frac{\rho}{\bar{N}} \int_0^\infty \exp[N(\epsilon/T - \epsilon/T_a)^2 - N/\bar{N}] dN \quad (11)$$

$$\sim \frac{(\rho/\bar{N})}{\bar{N}^{-1} - (\epsilon/T - \epsilon/T_a)^2} \quad T_e < T < T_a. \quad (12)$$

Below T_e ρ_a is infinite.

$$T_e = \frac{T_a}{1 + \bar{N}^{-1/2}(T_a/\epsilon)}. \quad (13)$$

For an exponentially distributed polydisperse mixture of polymer chains the adsorbed density diverges continuously; the density diverges unlike finite monodisperse chains and it does so continuously, not via a jump as monodisperse infinite chains do. The divergence occurs at a temperature T_e which is below the adsorption temperature of infinite chains by an amount proportional to $\bar{N}^{-1/2}$.

The divergence is also present for a distribution function $x(N)$ which is an exponential times a power law, as the Schulz distribution function is [1, 10]. Indeed the behaviour is qualitatively unchanged if the exponential is multiplied by any function of N which varies more slowly than exponentially, allowing the exponential dependence to dominate at large N . See ref. [1] for different distribution functions found for linear polymers.

All the above is for ideal polymers. What about polymers with monomers which repel each other, the standard model of a polymer in a good solvent? The free energy of adsorption of *isolated* polymer chains with monomers which repel each other again has a dominant linear term in N although the dependence on T is different [4, 6]. An exact field-theory treatment yields for long chains with repulsive monomer–monomer interactions [4, 6]

$$\frac{\Delta F(N)}{T} \sim -N(\epsilon/T - \epsilon/T_a)^{1/\Phi_0} \quad T < T_a, \quad (14)$$

where T_a is the adsorption temperature for interacting chains and again this is the part of the adsorption free energy which dominates when the free energy of adsorption is negative and has a magnitude much larger than unity. The exponent Φ_0 is estimated to be 0.59 [6]. So, ΔF is linear in N as before and so isolated chains with repulsive monomer–monomer interactions behave in qualitatively the same way as ideal chains. The non-ideal chains must, however, be isolated, i.e., so dilute even at the wall that the

interaction between chains is negligible, for this result to hold. Interactions between chains changes the free energy of adsorption and so the adsorption behaviour.

There is a thermodynamic transition only if the distribution $x(N)$ decays to zero only at $N = \infty$. If there is some maximum chain length N_c beyond which the distribution is cutoff, $x(N) = 0$ for $N > N_c$, then the transition is rounded off. For $N_c \gg \bar{N}$, the normalisation of the distribution is almost unaffected by the cutoff and we can estimate ρ_a by simply replacing ∞ by N_c as the upper limit of integration in eq. (11)

$$\rho_a \sim \frac{(\rho/\bar{N})}{\bar{N}^{-1} - (\epsilon/T - \epsilon/T_a)^2} \left\{ 1 - \exp\left(\left[(\epsilon/T - \epsilon/T_a)^2 - \bar{N}^{-1}\right] N_c\right) \right\} \quad T < T_a, \quad (15)$$

which can also be written as

$$\frac{\rho_a}{\rho} \sim \frac{1}{1 - \bar{N}(\epsilon/T - \epsilon/T_a)^2} \left\{ 1 - \exp\left(\left[\bar{N}(\epsilon/T - \epsilon/T_a)^2 - 1\right] \frac{N_c}{\bar{N}}\right) \right\} \quad T < T_a. \quad (16)$$

The adsorption only depends on two parameters, $\bar{N}(\epsilon/T - \epsilon/T_a)^2$ and N_c/\bar{N} .

There is no transition but for not too small \bar{N} and $\epsilon/T - \epsilon/T_a$, we see that the adsorbed density ρ_a increases as $\sim N_c(\epsilon/T - \epsilon/T_a)^2$. This should be compared with the corresponding expression for monodisperse chains, eq. (6). The increase in adsorbed density when the polymer is polydisperse is as fast as for monodisperse polymer of length N_c , equal to the longest chains present in the polydisperse polymer. This is perhaps surprising, *a priori* we might have thought that the adsorbed density increases about as fast as monodisperse chains of length equal to the average length \bar{N} . In fact polydisperse chains have a much higher adsorbed density than monodisperse chains with the same average length \bar{N} length. This is shown in fig. 1, where the slope of the adsorbed density for polydisperse chains (dashed curve) as a function of the attraction energy over the thermal energy is very similar to that of monodisperse chains with the length N_c (dot-dashed curve) and much larger than that of monodisperse chains with the average length \bar{N} (solid curve).

Physically, what is happening is that most of the adsorbed monomers are from the largest chains of the distribution. That most of the adsorbed monomers are from the longest chains can be seen if we recall that the contribution to the adsorbed density of chains ρ_a from chains of length N is given by the integrand of eq. (11). For a cutoff distribution below the T_e of a non-cutoff distribution with the same \bar{N} , the integrand is an increasing function of N .

To summarise, polydisperse ideal polymer chains show three qualitatively different adsorption behaviours depending on the large N tail of the distribution function $x(N)$:

(A) $x(N)$ decays more slowly than exponentially in the $N \rightarrow \infty$ limit, then the mixture behaves like infinite monodisperse chains; (B) $x(N)$ decays exponentially in which case the adsorption density diverges continuously, and (C) either $x(N)$ decays more rapidly than exponentially or is cutoff at some maximum chain length, in which case the mixture behaves like finite monodisperse chains.

To conclude, we have been able to classify polydisperse polymer solutions into three classes, depending on their adsorption behaviour. The case of an exponentially decaying distribution of chain lengths is especially interesting as it behaves in a way which is qualitatively different from that of monodisperse chains. Sharp distinctions between monodisperse and the different polydisperse distributions can only be drawn when there are infinite chains present. Only then is a phase transition possible whose presence or absence can be used to assign unambiguously a distribution to one of the classes. However, at least when the polydisperse distribution function $x(N)$ decays exponentially, even when the distribution is truncated beyond some finite value N_c there is a remnant of the behaviour of the untruncated distribution. Near the temperature T_e where the adsorbed density of the untruncated distribution would diverge there is changeover in behaviour: above T_e the shortest chains contribute most to the adsorbed density ρ_a , below it the longest chains contribute most.

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Figure Caption

Fig. 1. The adsorbed density ρ_a at the wall is plotted as a function of the attraction energy over the thermal energy minus its value at the adsorption transition for infinitely long chains. The solid and dot-dashed curves are for monodisperse chains of lengths $N = 50$ and 150 , respectively. The dashed curve is for polydisperse chains distributed according to an exponential distribution of sizes with an average chain length $\bar{N} = 50$ and maximum chain length $N_c = 150$. At small $\epsilon/T - \epsilon/T_a$ the adsorbed density for the polydisperse polymer is less than that for monodisperse polymer of length $N = 50$.

